V and N doping on the surface of TiO₂: DFT-GGA study

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Keywords: DFT+U, TiO₂, co-doping

Introduction

Theoretical chemistry studies are useful to contribute to a better understanding of atomic-scale systems. Through molecular modeling and calculations based on DFT, it is possible to describe theoretically some properties, chemical bonds, as well as the electronic structure of systems of interest. This area of knowledge finds applicability in photocatalytic studies that fit into a set of processes called Advanced Oxidative Processes (POAs). These processes promote the degradation of pollutants through oxidizing agents, in the presence of activated catalysts. Among the catalysts used in the photocatalytic process, the anatase titanium dioxide catalyst stands out for its applicability. However, there are some limitations, mainly the low adsorption energies. One way to contour this situation is the doping of the catalysts, which can be accomplished through a cationic and anionic monodoping or through a co-doping, which can be cationic-cationic, anionic-anionic or cationic-anionic.^{1,2,3}

Methodology

All calculations were performed using VASP software (Vienna Ab initio Simulation Package) with version 5.4.1. The DFT method was used at Generalized Gradient Approximation (GGA) with the Perdew-Burke-Ernzerhof functional (PBE). The cutoff energy value was set to 300 eV and the K-points to 3x3x1. The surface of TiO₂ (101) is formed by 144 atoms. The substitutional atoms of vanadium and nitrogen were inserted into the outer layer according to Figure 1.

Figure 1 – Site positions of doping process

Results and Discussion

First, it was analyzed the vacancy position in the supercell, according to the Figure 1. The results observed in monodoping with vanadium showed that there was no significant difference (<0.002 eV) in a substitutional doping at P1, P2 and P3 sites, which was expected due to the symmetry of these points, and all atoms in this alignment are hexacoordinated. Monodoping with nitrogen showed that there was no significant difference (<0.01 eV) in a substitutional doping at the atoms contained in the same line.

In the V_{Ti} - N_O codoping, the dopant structures bonded together are more stable than the unbound dopant structures. Between the positions P1 and P2, the position P1 presented the smallest energy of the slab. Analysis of molecular electrostatic map, charge of atom sites, and electron localization function was also performed.

Final Remarks

The analysis of the different dopants performed for the study allowed the determination of the best substitution doping positions for V_{Ti} and N_O monodopates and V_{Ti} - N_O co-doping.

Acknowledgment – CAPES, CNPQ, FAPDF.

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